AD NUMBER
AD469132
LIMITATION CHANGES
TO: Approved for public release; distribution is unlimited.
FROM: Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; AUG 1965. Other requests shall be referred to Air Force Materials Lab., Wright-Patterson AFB, OH 45433.
AUTHORITY
AFSC/IST ltr 21 Mar 1989

AFML-TR-65-2
PART III, VOLUME I

TERNARY PHASE EQUILIBRIA IN TRANSITION METAL-BORON-CARBON-SILICON SYSTEMS

PART III. SPECIAL EXPERIMENTAL TECHNIQUES
VOLUME I. HIGH TEMPERATURE DIFFERENTIAL THERMAL ANALYSIS

H. D. HEETDERKS
E. RUDY
T. ECKERT

AEROJET-GENERAL CORPORATION

AF33(65)-1249

TECHNICAL REPORT No. AFML-TR-65-2, PART III, VOLUME I

AUGUST 1965

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified users may obtain copies of this report from the Defense Documentation Center.

The distribution of this report is limited because it contains technology identifiable with items on the Mutual Defense Assistance Control List excluded from export under U. S. Export Control Act of 1949, as implemented by AFR 400-10.

Copies of this report should not be returned to the Research and Technology Division unless return is required by security considerations, contractual obligations, or notice on a specific document.

TERNARY PHASE EQUILIBRIA IN TRANSITION METAL-BORON-CARBON-SILICON SYSTEMS

PART III. SPECIAL EXPERIMENTAL TECHNIQUES
VOLUME I. HIGH TEMPERATURE DIFFERENTIAL THERMAL ANALYSIS

H. D. HEETDERKS
E. RUDY
T. ECKERT

FOREWORD

This report was prepared by the members of the Materials Research Laboratory, Aerojet-General Corporation, Sacramento, California under USAF Contract No. AF 33(615)-1249. The data presented in the experimental section of this report were obtained from work under this program.

The project, which includes the experimental and theoretical investigation of selected binary and ternary systems in the system classes Me_1-Me_2-C, $Me-B-C$, Me_1-Me_2-B, $Me-Si-B$, and $Me-Si-C$ was initiated on 1 January 1964 under Project No. 7350, "Refractory, Inorganic Non-Metallic Materials", Task No. 735001, "Non-Graphitic". The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Captain R. A. Peterson acting as Project Engineer, and Dr. E. Rudy, Aerojet-General Corporation as Principal Investigator.

The authors are grateful to Dr. S. Langer, General Atomic, San Diego, California, who helped with technical advice in the initial design stages of the apparatus. The assistance of Mr. D. P. Harmon in performing the measurements is acknowledged.

The manuscript of this report was released by the authors April 1965 for publication as an RTD Technical Report.

FOREWORD (Cont'd)

Other reports issued under USAF Contract AF 33(615)-1249
have included:

Part I. Related Binaries

Volume I, Mo-C System

Volume II, Ti-C and Zr-C System

This technical report has been reviewed and approved.

W.G. RAMKE
Chief, Ceramics and Graphite Branch
Metals and Ceramics Division
Air Force Materials Laboratory

ABSTRACT

A high sensitivity differential thermal analysis apparatus, capable of operating to temperatures of 3600°C under controlled time-temperature conditions, is described.

Measurements on binary and ternary carbide systems revealed a number of previously undetected phase reactions. With the exception of V_2C, all subcarbides of the refractory transition metals undergo isothermal phase changes at high temperatures. The lower temperature stability limits of the high temperature phases in the systems Mo-C and W-C were determined. Similar to the corresponding system with oxygen, the α-modification of hafnium is stabilized to higher temperatures by carbon additions, while the α-β-transformation in titanium and zirconium is affected to a moderate extent only.

The application of DTA-techniques to the investigation of non-variant equilibria involving a liquid phase and to the study of reaction kinetics (disproportionation of solid solutions, reactions along non-equilibrium paths, reactions involving order-disorder phenomena) is discussed and examples are given.

(37 pp) (21 fig.) (1 tbls..) [40 ref.)

iv

TABLE OF CONTENTS

ILLUSTRATIONS

ILLUSTRATIONS (Cont'd)

TABLES

I.   INTRODUCTION AND SUMMARY

In recent years, the demand for materials capable of operation at
very high temperatures has increased rapidly and in turn has stimulated
the development of improved techniques for the study of phase reactions
at high temperatures.

While the gross features of an alloy system can be delineated fairly
well, using the commonly accepted technique of X-ray and metallographic
analysis on equilibrated and quenched alloys, rapid high temperature phase
reactions (c.f. phase transformations, precipitation and dissolution
reactions) are likely to escape experimental observation. The location
of transformation temperatures by metallographic means is a quite cumber-
some procedure and extreme care must be exercised in the interpretation
of such indirect evidence.

During the past year, increasing difficulties encountered in the
experimental investigation of the high temperature phase-relationships in
refractory alloy systems in this laboratory resulted in the development
of a Pirani-type melting point furnace of improved design and a high tempera-
ture differential thermal analysis (DTA) apparatus. Since then, these
apparatus have proven to be invaluable aids for the elucidation of the phase
reactions occurring at very high temperatures.

In this paper, the DTA-apparatus and its application to the study of
the phase relationships in refractory carbide systems will be discussed,
while the melting point furnace will be the subject of a subsequent
publication[1]. Brief descriptions of both apparatus have been given in
earlier reports[2, 3].

1

II.   PRINCIPLE OF OPERATION - LITERATURE REVIEW

The application of differential-thermoanalytical techniques to metallurgical problems is old[4-8] and a large number of devices, both for qualitative as well as for quantitative applications have been described in the literature[9-13].

The principle of differential thermal analysis is extremely simple: A piece of sample material, along with a similar piece of material known to undergo no phase changes is heated at a controlled rate in a furnace. If at some temperature the sample undergoes an isothermal reaction which involves an enthalpy change, the temperature of the sample will tend to remain at T_o, while the temperature of the inert sample continues to rise. Thus, a reaction associated with a heat effect generates a difference in temperature between the sample and the reference body. This difference is detected and recorded. After the reaction is completed, the sample tends to approach the environmental temperature (i.e. the temperature of the reference sample).

DTA-apparatus for higher temperatures have been developed by T. F. Newkirk[14] (1550°C), H. J. Borchardt[15] (1750°C), and by M. M. Hopkins[16] (1500°C). Practically all of these designs use thermocouples as the temperature-sensing elements, although the use of thermistors in connection with a low-temperature apparatus has also been described[17].

Apart from the limitations imposed by the specific furnace design, an upper temperature limit for thermocouple-operated devices is also set by their interaction with test or container material, and change of the

2

output - temperature characteristics of the thermocouples after exposure to high temperatures also may cause problems and necessitate frequent recalibration or replacement.

An improved design of this type was recently reported by R.V. Sara and R. T. Dolloff[18]. Using graphite/boronated graphite thermoelements they were able to carry out DTA-measurements at temperatures in excess of 2500°C.

A high temperature DTA-apparatus with infrared detectors at the temperature sensors was proposed by S. Langer at General Atomic[19] and applied to phase studies in excess of 2000°C. Test and reference sample, both of which are contained in a crucible, are heated in the field of an eddy current concentrator. Radiation from reference and test sample is focussed onto separate lead sulphide infrared detectors, and the difference in output, after amplification, is recorded. Difficulties arise from the poor matching characteristics of the semi-conductor devices, giving rise to excessive base-line drifting[19]. A similar design was recently described by G. N. Rupert[20]. A photomultiplier tube serves as the temperature sensor, and temperature versus time curves are displayed either on a cathode ray oscilloscope or on a stripchart recorder.

III.   DESIGN CONSIDERATIONS

From considerations regarding reliability of operation and versatility in use, direct resistance heating seemed to be more promising than R. F. - heating and therefore this method was chosen in the design of our furnace. A proven heater configuration was available from the hot-press design of

3

Metallwerk Plansee, A.G., Reutte, Tirol, Austria, and was adopted with only minor modifications.

From the accuracy and sensitivity point of view, it seemed preferable to separate the ΔT-detection from the temperature measuring system, i.e. to measure DTA curves, rather than heating and cooling curves as in the design of G. N. Rupert[20]. Since the use of thermocouples was prohibited from compatibility considerations, photo diodes were chosen as the temperature sensing elements in the ΔT-detection system. The matching problem of the radiation sensors was overcome by using only one photo diode in conjunction with a mechanical chopping device for the detection of the temperature difference between test and reference sample. The chopper, which has the shape of a semicircle, alternately interrupts the radiation coming from the reference and test sample. Thus, the photo diode alternately views the reference and test body (radiation comparison principle). After amplification and detection, the signal is used to drive one channel (ΔT-axis in the DTA-thermogram) of an X-Y recorder.

For the measurement of the sample temperature, an electronic pyrometer was selected. Its output, which is a known function of temperature, drives one channel (T-axis in the DTA-thermogram) of the X-Y-recorder, and is also used as comparison signal for the temperature control system. An overall view of the DTA-setup is shown in Figure 1.

4

Figure 1. Overall View of the DTA-Apparatus

A. Radiation Detection Head

B. Control Panel

C. X-Y-Recorder

IV. PHYSICAL SETUP

A. FURNACE AND RADIATION DETECTION SYSTEM (Figure 2)

The sample (N) is a small cylinder (14 mm dia x 16 mm high) with a concentric black body hole (4 mm dia x 10 mm deep) at one end. The specimen is placed, along with a reference specimen (FF) of the same dimensions, in a container (GG). Test and reference sample are made ?s symmetrical as possible in order to keep base-line drifting effects, due to uneven heating, to a minimum. Erroneous readings due to surface reflections are avoided by placing a series of radiation shields (EE) on top of the sample container. The sample container, which can be made from graphite or some other suitable material, is placed inside a cylindrical graphite heater (CC), which is mounted between two graphite retainers (BB and II). The whole assembly, shown in exploded form in Figure 3, is clamped between two water-cooled (DD and JJ) copper electrodes (AA and KK) by means of the upper retainer, which is threaded into the upper electrode. For very high temperature runs, the heater is surrounded by graphite wool (HH) for insulation. The lower electrode is provided with flexible water and power connections to allow for thermal expansion of the heater. The whole assembly is enclosed in a stainless steel chamber, which can be operated either under vacuum or under inert gas to 6 atmospheres pressure.

Radiation passes from the specimen and the reference body to the temperature measuring portion of the apparatus through four water-cooled (I and Y) sight tubes (J), spaced symmetrically about the center line. At the end of each sight-tube is a quartz window (W). To prevent clouding
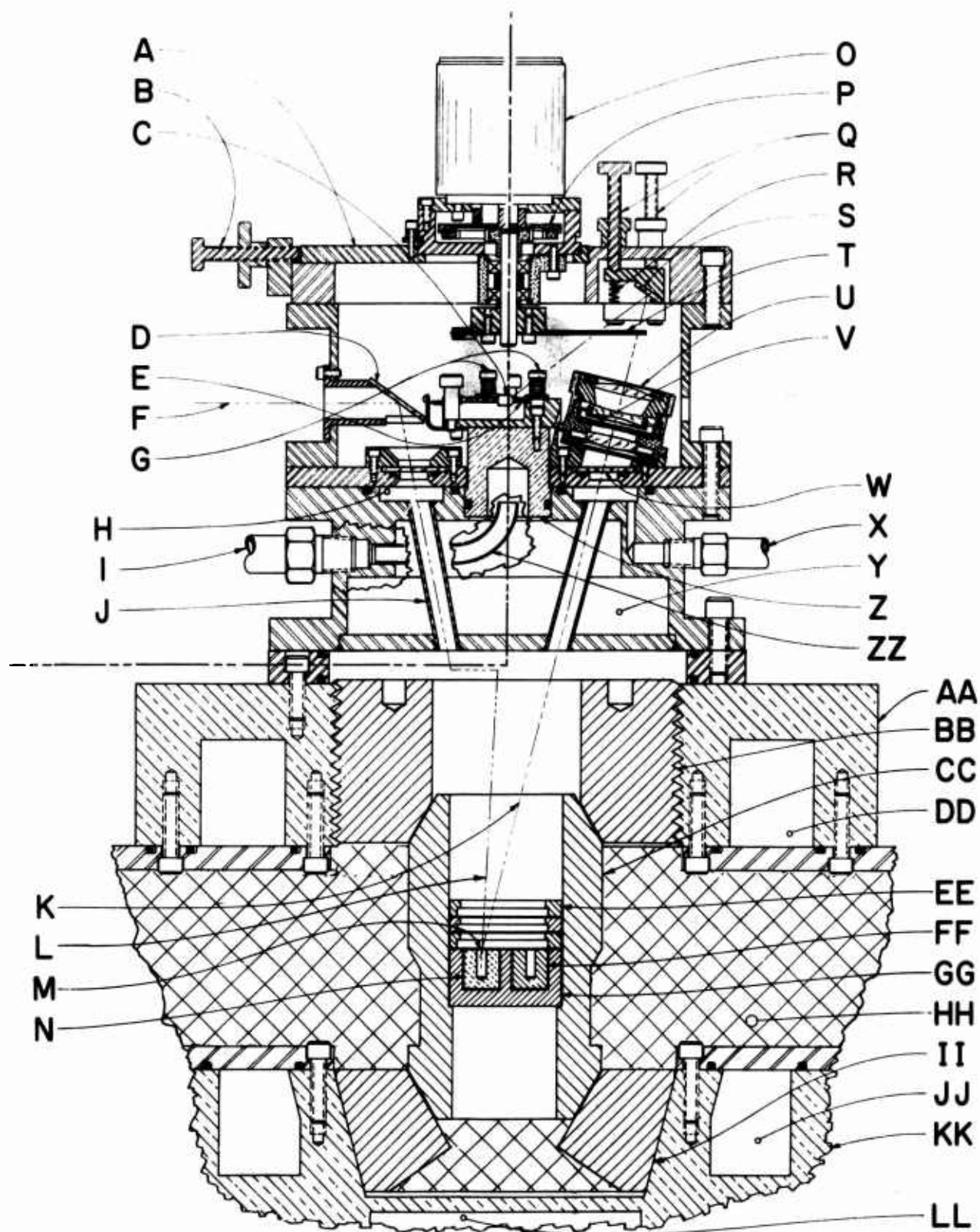
Figure 2. Furnace and Radiation Detection System of the DTA-Apparatus
(Legend in the Text)

— .. — .. — Section Rotated 90°

of the windows at high temperatures, an annular channel (H) is provided

between the windows and the sight tubes, through which inert gas can be

passed (X).
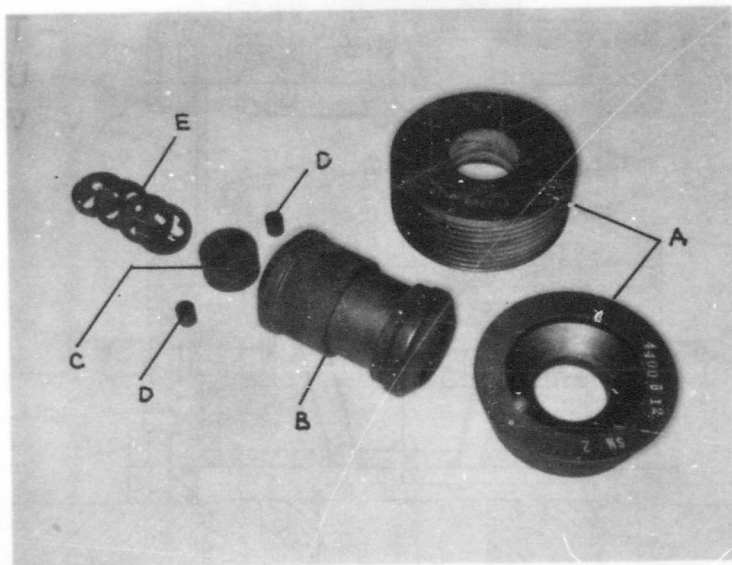
Figure 3. Exploded View of the Heating Assembly of the
DTA-Apparatus

A. Graphite Retainers   D. Reference and
B. Heater   Test Sample
C. Sample Container   E. Radiation Shields

For the measurement of the sample temperature, above

two of the sight tubes, mirrors (D) are mounted, which view the sample

along the optical paths (F-L). One of these paths terminates in an electronic

radiation thermometer (Thermodot model TD-6BT-70). The other path is

used for following visually the temperature during the experiment with a

micropyrometer. The output of the Thermodot, which is a known function

of temperature, is fed directly into one channel of the X-Y-recorder.

The other two sight tubes (J) are used in the ΔT-detection

system. Radiation from the specimen passes along optical path (K) through

one of the sight tubes and the quartz window to the lens system (U), where
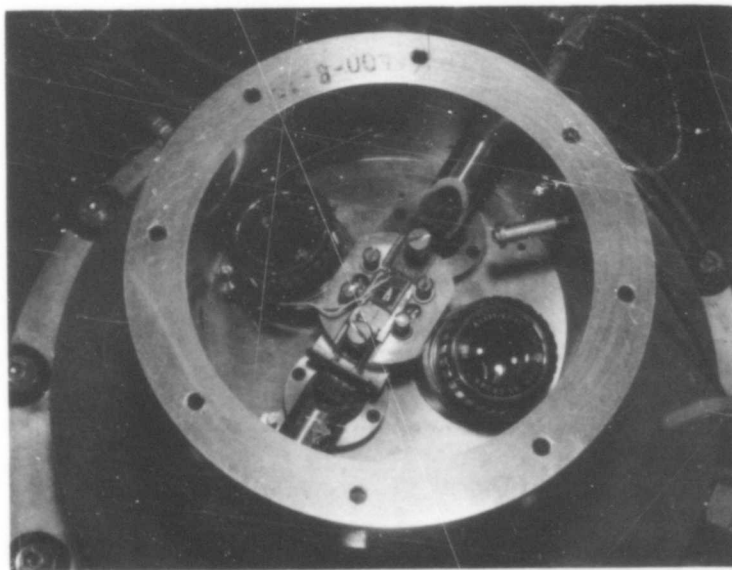
Figure 4. Top View of the Optical and Radiation Detection
System.
(Top Cover with Semicircle Removed)

an image of the black body hole of the specimen is focussed and reflected

by a mirror (S) onto a photo diode (C). An analogous lens-mirror system

(Figure 4), spaced 180° from the one shown, focusses an image of the

black-body hole in the reference specimen onto the same photocell. For

adjusting purposes, the photo diode is mounted on a movable sled (E) which is held in place by spring-loaded fastening screws (G). Mounted on the same sled is a target which can be slid in the place of the photo diode and serves as a centering aid for the black body images. The mirrors (S) are provided with adjusting screws (Q) to enable the black body images to be exactly superimposed.
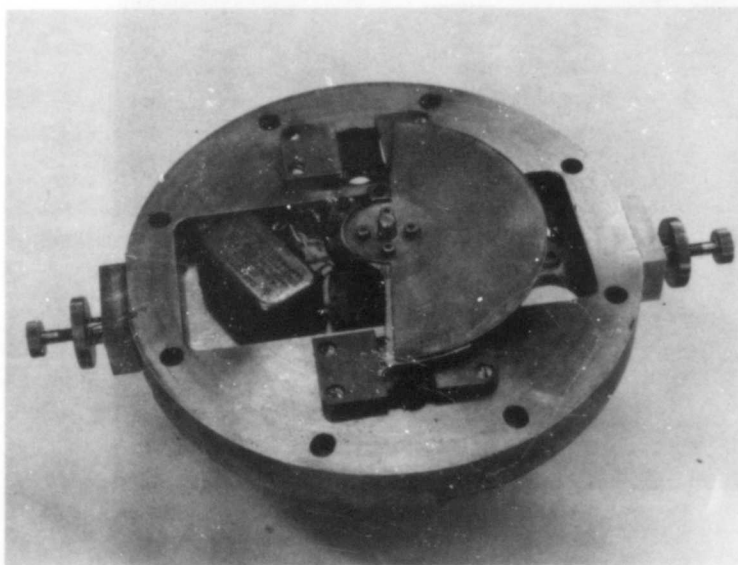
Figure 5. Mechanical Radiation Chopping Device

For control of the amount of radiation falling on the photo-cell, the lens systems are equipped with adjustable apertures (V). Between the two paths, a semicircular chopping device (T, Figure 5) is mounted. The mirrors direct the paths through the rotating semicircle, which

alternately interrupts the radiation from reference and test sample to
the photocell. Thus, as the chopper rotates, the photo diode alternately
views the black body holes of the test and reference sample.
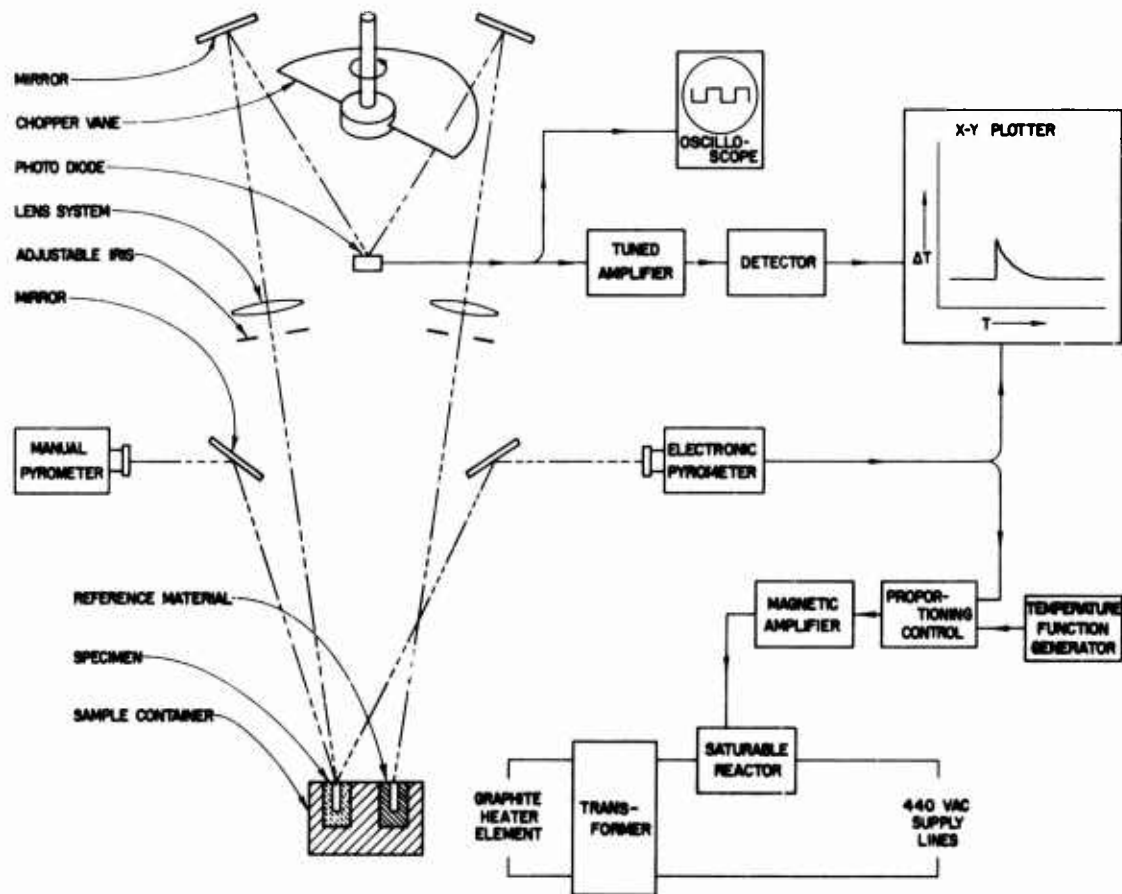
Figure 6. Experimental Setup for DTA-Measurements at
High Temperatures (Schematic)

The sector is driven at 5400 rpm by a synchronous motor
(O) via a gear train (P). Motor and semicircle assembly are fastened
to a mounting plate (A), which can be adjusted by screws (B).

The electronic portion of the apparatus is divided into two parts: The detection and measurement of the temperature difference between reference and test sample, and that concerned with the temperature control of the furnace.

The output of the photo diode is a 90 cps square wave, the amplitude of which is a function of the temperature difference between reference and test sample. Since there is considerable 60 cycle interference due to the heavy AC currents used to heat the furnace, the signal from the photo diode has to be filtered, so that only the desired ΔT-information is passed through. To accomplish this, the photo diode output is fed through a tuned amplifier with a Twin-T circuit tuned to 90 cps connected in its feed back loop. The band pass of the system is three cycles. The amplifier output, which consists of a 90 cps sine wave with the amplitude approximately proportional to ΔT is then passed through a half-wave diode detector. The resulting DC-signal is used to drive the ΔT-axis of the recorder.

An important feature of the DTA-apparatus is the time-temperature control:

A variable speed DC-motor rotates a Helipot through a gear train (temperature function generator in Figure 6), producing a controlled variable set-point. The output from the Helipot along with that from the Thermodot is fed into an error amplifier. The amplified signal controls a magnetic amplifier/silicon controlled rectifier system, which drives the saturable core-reactor and which ultimately controls the power delivered to the heater.

Both heating and cooling rates, marked on a calibrated dial, are adjustable to fractions of a degree per second. The maximum heating rate obtainable is approximately 20°C per second, the maximum controllable cooling rate (with insulation) is approximately 14°C per second.

B. SENSITIVITY

A further important characteristic of a DTA device is its sensitivity, i.e. the minimum heat quantity, which, at a given temperature, will produce a distinguishable signal. Obviously, this quantity is a function of many parameters, such as temperature, heating rates, heating geometries, thermophysical properties of sample and container material, characteristics of the temperature detection system, etc.

The sensitivity of the described apparatus in terms of these individual parameters has not been determined as such. However, back calculations from experiments on the solid-state transformations in the system Mo-C, where the approximate heat data are known from other sources, showed that an enthalpy change of 20 calories in the sample produced a minimum signal to noise ratio of about 20 ($T \sim 2000°C$). Similarly, by using the known diode output —— temperature function for converting signal outputs to absolute temperature differences, it could be shown that a temperature difference of 1°C between test and reference sample (corresponding to approximately 1.5 cal for the particular material used, if under adiabatic conditions) produced a very clear and distinguishable signal (signal to experimental noise $\approx$ 6:1).

For the case that saturation phenomena in the photo detection devices have to be taken into consideration, the temperature will

13

exert a strong influence on the observed overall sensitivity of the apparatus. In the described setup, a RCA 7224 photodiode is used. Without filtering, this diode as used in our optical configuration has a sensitivity of approximately 0.08 mV. $°C^{-1}$ over the temperature from 1000 to 2500°C. Above 2500°C a slight dropoff is observed, while the output approaches zero below approximately 600°C. Infrared detectors (c.f. for example Kodak's Ektron detectors) in conjunction with infrared-transparent windows will be preferable to the combination quartz-photo diode at temperatures below 600°C. (Low intensity of shorter wave length radiation, strong absorption of quartz in the near infrared). On the other hand, at these low temperatures, use of the well-established thermocouple operated devices may seem to be preferable.

Generally, signals corresponding to fast processes can be augmented by increasing the heating or cooling speeds. Slower processes are characterized by a dependence of the observed reaction temperature upon the heating and cooling rates and the overall sensitivity will in this case be a maximum at some intermediate rate.

C.   SIGNAL INVERSION

The sample temperature relative to that of the test body, indicative of an exothermic or endothermic relation is followed on the screen of an oscilloscope during the run and marked. Since the electronic system as described measures the absolute value of the temperature difference between reference and test body, the relative direction the signal will take will depend on the (arbitrary) setting of the temperature difference at start. This arbitrary difference is set by means of the adjustable apertures in the

lens system. If both the heating and cooling curves are run under the same conditions (for example, with ΔT set such, that $T_{sample} - T_{ref.body}$ remains either >0 or <0 throughout the experiment), the peaks on the heating and cooling cycle will appear inverted. If the sign differs, exo- and endothermic reactions will produce signals pointing in the same direction. Since there is no doubt regarding the relative temperature changes, for easier recording and comparison purposes, the DTA-thermograms are often recorded with changed signs of the ΔT-axes.

D.   CAPABILITIES AND LIMITATIONS

The temperature limitations of the furnace itself are imposed by the sublimation of graphite. Although the diffusion of carbon vapor can be slowed down by application of higher inert gas pressures, the lifetime of the heating element is limited to seconds at 3800°C. The maximum safe operating temperature is approximately 3600°C.

A problem, which in many cases limits the applicable temperature range for the investigations, is presented by the interaction of the sample with the container material, and special precautions (change of container material, wall linings, top covers, etc.) have to be taken to prevent errors in the interpretation of the results.

E.   TEMPERATURE CALIBRATION

The correction to be applied to the measured temperature is given by

$$\Delta T_{corr} \simeq -T_m^2 \cdot \frac{C_2}{\lambda} \ln T_r \tag{1}$$

15

where T_r designates the total transmission of the optical system including the correction due to non-black body conditions, C_2 is a universal constant, $C_2 = \frac{h \cdot c}{k} = 1.4384$ [cm.deg], and T_m is the measured temperature. From the apparent temperatures of a black radiation source of known temperature the total transmission of the optical system was determined to be $T_r = 0.841$. With this value, the corrections to be applied to the readings can be calculated from equation (1). The total transmission, translated as emissivity, is also used for setting the adjustable emissivity dial of the electronic pyrometer.

F.   OPERATION

After insertion of the loaded sample container into the heater assembly, the radiation detection system is fastened to the top of the furnace and the chamber evacuated. After several inert gas purges, the furnace is brought to temperatures of 500 - 1000°C. After the final adjustments on the ΔT and T-detection system (focussing of black body hole images, balancing of the semicircle, focussing of the electronic pyrometer onto the black body hole of the test specimen) have been made, the desired heating or cooling rate is preset on the calibrated dial and the temperature function generator activated. After equilibration of the sample at the selected conditions the temperature range of interest is scanned for possible reactions. The temperature of the sample is followed independently with a micropyrometer through one of the observation ports and additional temperature control marks checked off on the recorder chart during the runs.

For adjusting and monitoring purposes, as well as the determination of the sign of the temperature change (endothermic or

16

exothermic) the square wave output is continuously displayed on the screen
of an oscilloscope during the experiment.

CONCENTRATION

E   Eutectic Composition
e   Eutectic Line
V   Intermediate Phase
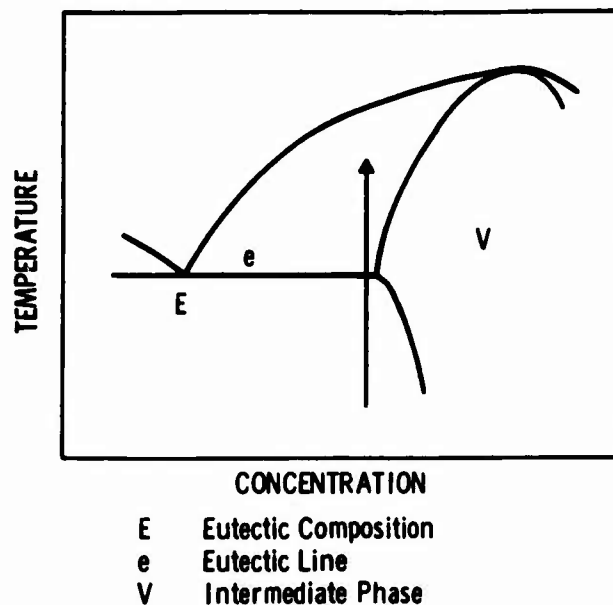
Figure 7.   "Restschmelze" - Method for the Determination
            of the Eutectic Line by Differential Thermal
            Analysis (Schematic)

The investigation of isothermal reactions involving a liquid
phase naturally presents a somewhat greater problem because of the en-
hanced interaction rate with the container material. On the other hand the
"Restschmelze"- method often allows the location of eutectic or peritectic
temperature lines in even unfavorable cases and also provides in this way
a very valuable tool for the determination of the homogeneity limits of
phases. A schematic illustration of the conditions underlying this method
is sketched in Figure 7 and is self-explanatory. Due to the presence of
only small amounts of liquid, the physical shape of the test specimen remains

unchanged and the large heat capacity of the inert solid phases results in sharp and confined peaks.

V.   APPLICATIONS

A.   THE α-β-TRANSFORMATION OF HAFNIUM

The experimental alloy material was prepared by remelting sponge-hafnium (Wah Chang Corp., Albany, Oregon,) main impurities: 4 At% Zr, < 0.4 At% O) several times in an electron-beam furnace (Heraeus Es 2/4). The resulting bars were then fabricated into samples of the required size. DTA-runs were performed under vacuum as well as under high purity helium (3 atm). The results were identical.

A sharp thermal arrest was found to occur at 1800 ± 15°C (Figure 8). Using the correction suggested by D. K. Deardorff and H. Kato[21] a value of 1840 ± 25°C is extrapolated for pure hafnium.

This value agrees very well with the determinations by N. J. Grant and B. C. Giessen[22], but less favorably with the presently accepted value of 1950° - 1990°C[23, 25]. A summary of previous determinations is given in Table 1.

B.   EFFECT OF CARBON ON THE α-β-TRANSITION OF HAFNIUM

The attack of this problem seemed particularly interesting, since stabilization of the α-modification to higher temperatures has been found for other interstitial atoms, such as oxygen[28] and nitrogen[29].

Recent investigations carried on at the U. S. Bureau of Mines[30] indicated a moderate effect of carbon on the α-β-transformation of hafnium only, although comparatively large solubilities (~10 At%) in

both modifications have been found. Analogous results were reported by R. V. Sara and C. E. Lowell[31] in a very recent investigation, whereas the work by R. G. Avarbe, et.al.[32] would indicate stabilization of the α-modification to high temperatures, and only a very nominal solubility of carbon in the body-centered cubic form.
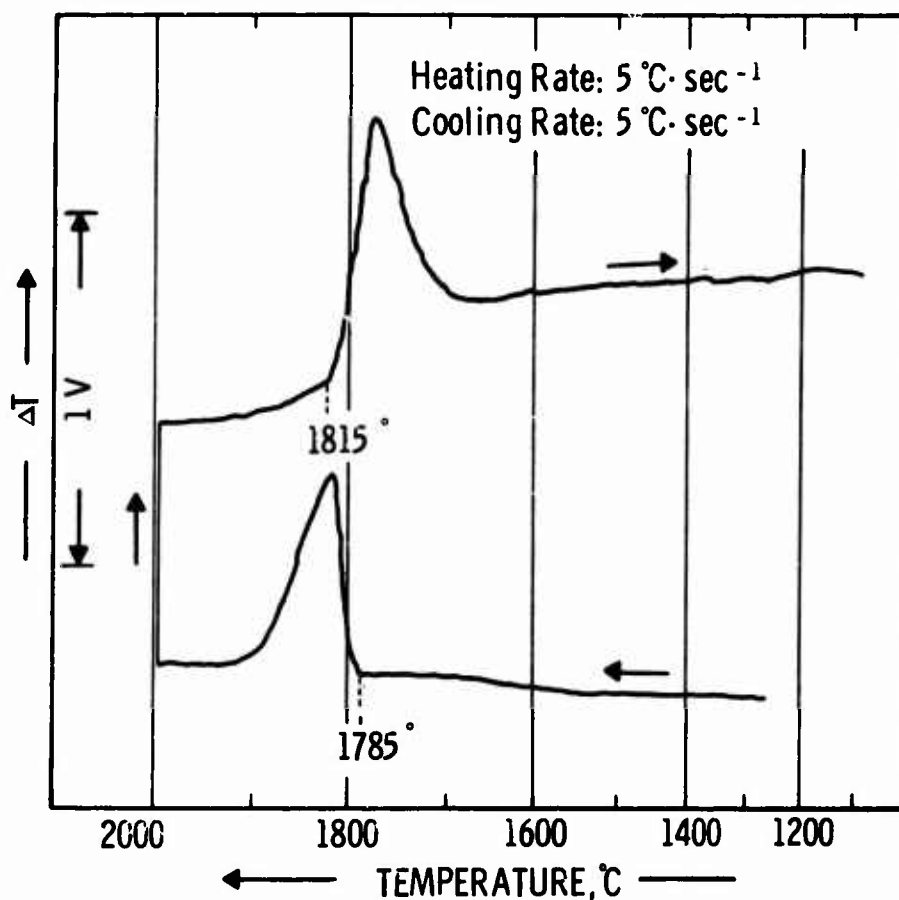

Figure 8. Differential Heating and Cooling Curve of a Hafnium - 4 At% Zirconium Alloy

The experimental studies were carried out using the same starting material as described in the previous section. To delineate the features in the metal-rich portion of the hafnium-carbon system, the sample

Table 1. Temperatures of the α-β-Transformation in Hafnium

Author	Ref	Transf. Temp. °C	Remarks
Zwikker, 1926	26	1327° to 1527°	-
Duwez, 1951	27	1310°	-
Fast, 1952	23	1950°	extrapolated to 100% Hf
Deardorff and Kato, 1959	21	1760° ± 35°	——"——
Taylor and Doyle, 1960, 1964	24	1950°	4.41 At% Zr
Grant and Giessen, 1960	22	1840°	4.41 At% Zr
Ross and Hume-Rothery 1963	25	1995 ± 70°	extrapolated to 100% Hf
Present Investigation	-	1800 ± 15°	4 At% Zr
	-	1840 ± 25°	extrapolated to 100% Hf

was repeatedly heated and equilibrated in a graphite sample holder, and differential heating and cooling studies were performed after each homogenization treatment. The first of the heating curves shown in Figure 9 corresponds to pure hafnium. With increasing carbon-pickup, the onset of the transformation is shifted to higher temperatures. After 16 runs, the peak corresponding to the transformation has practically vanished. The carbon concentration of the alloy obtained from a subsequent chemical analysis of the alloy was 1.9 At%. Above 2.0 At% carbon, no deviations from the normal course of the base line could be detected. The rapid increase of the transformation temperature upon incorporation of carbon atoms

20

into the lattice is also shown from the corresponding differential cooling curves, which give a better indication of the upper temperature limit of the transformation (Figure 10). The results of the DTA-investigations were
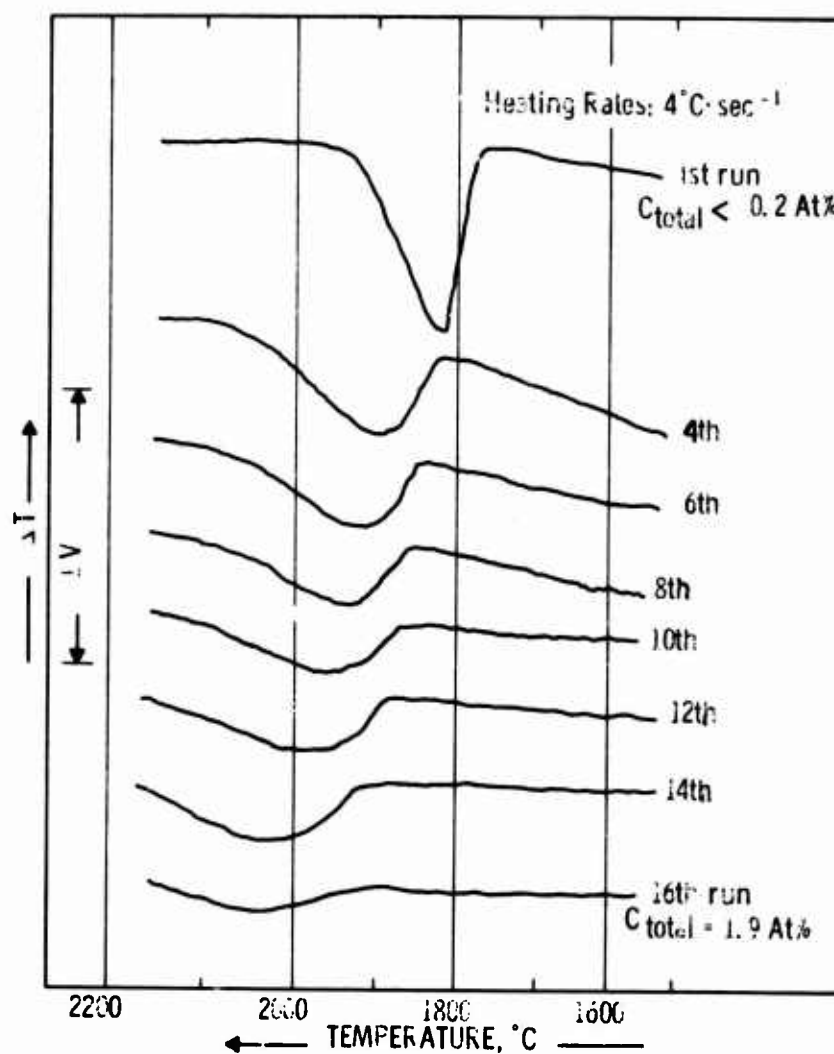
Figure 9. Differential Heating Curves of Hafnium - 4 At%
Zirconium after Repeated Exposure to Graphite

(Note: The Alloy was Held for 1 min at 2160°C Prior
to Each Subsequent Run)

independently confirmed by metallographic analysis of quenched alloy material[33] and are in favor of Avarbe's interpretation.
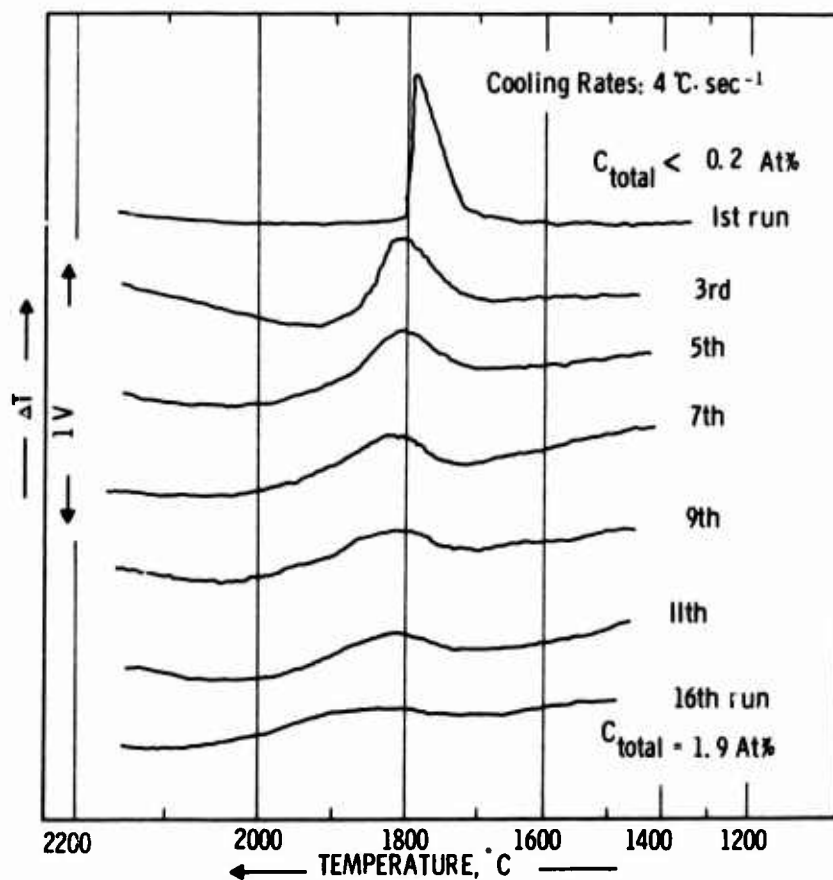

Figure 10. Differential Cooling Curves of the Sample Shown in Figure 9

It is interesting to note that although zirconium has a comparable atomic diameter, no significant change of the transition temperature could be detected (Figure 11 and 12). For titanium the observed change is somewhat larger (Figure 13).

C. PHASE TRANSFORMATIONS OF THE Me$_2$C-PHASES

In the investigation of binary and ternary carbide systems a number of previously unknown phase reactions have been found to occur at high temperatures. This applies especially to the subcarbide phases of the refractory transition metals, where for all but V$_2$C such phase-transitions have been found. The nature and thermodynamic interpretation of these phase reactions has been discussed by E. Rudy, et.al.[3]. Table 2 contains a summary of the observed temperatures for these isothermal reactions. While β-Mo$_2$C can be fairly easily retained by rapid
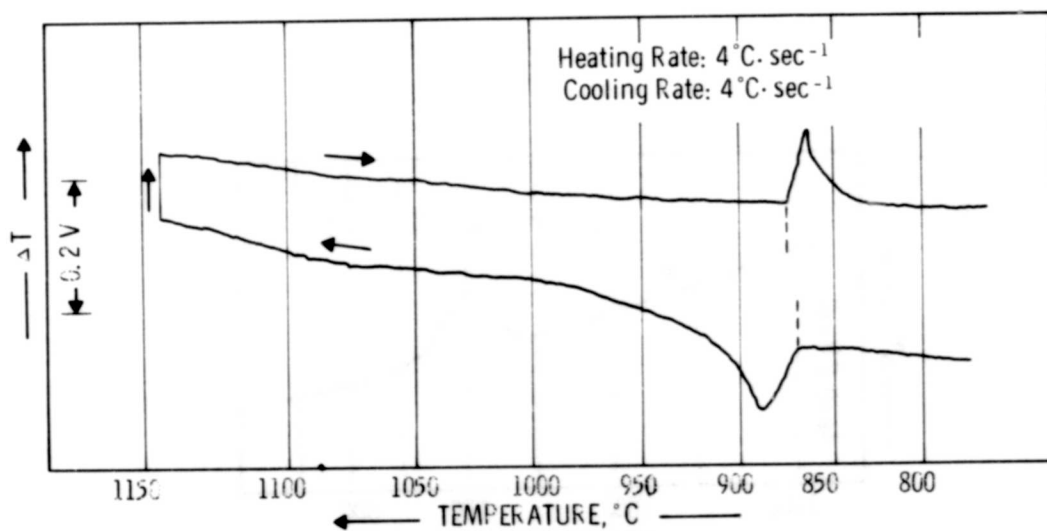

Figure 11. α-β-Transformation in Crystal Bar Zirconium

cooling, the corresponding β-modification of the other subcarbides decomposes very rapidly at the corresponding eutectoid temperatures as

23
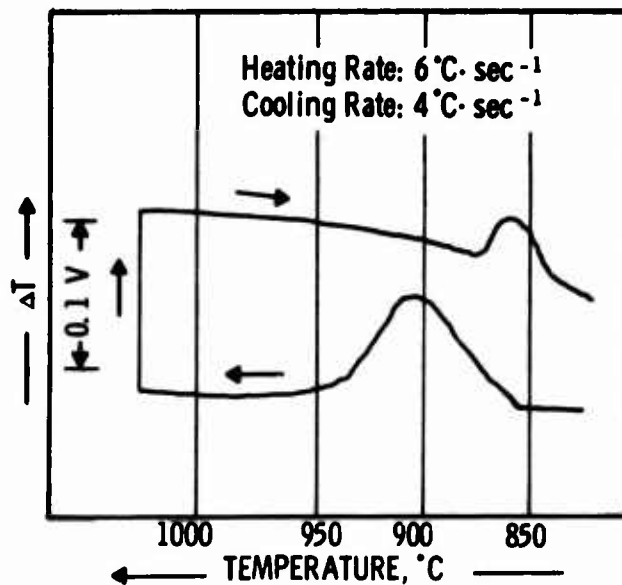
Figure 12. α-β-Transformation of Zirconium in a Zirconium
20 At% Carbon Alloy
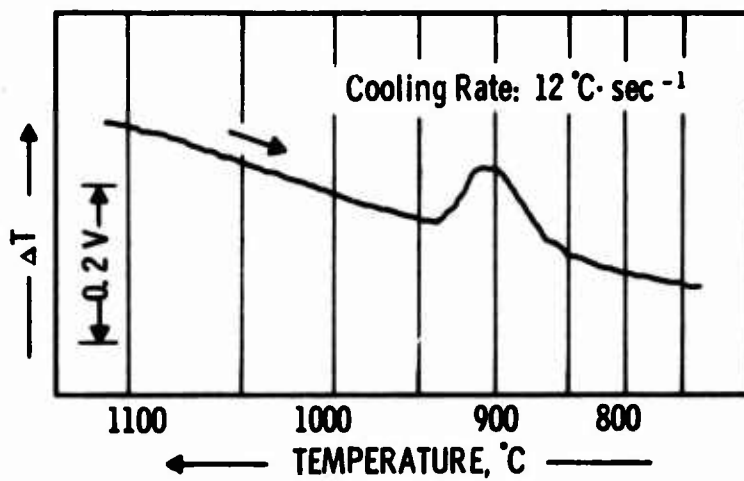
Figure 13. α-β-Transformation of Titanium in a Titanium-
20 At% Carbon Alloy

Table 2. Isothermal Reactions of Subcarbide Phases

Carbide	Temperature, °C	Reaction
Nb_2C	$2430 \pm 30°$	$\alpha\text{-}Nb_2C \rightleftharpoons \beta\text{-}Nb_2C$
Ta_2C	$2180 \pm 20°$	$\alpha\text{-}Ta_2C \rightleftharpoons \beta\text{-}Ta_2C + Ta$
	$1930 \pm 30°$	$\alpha\text{-}Ta_2C + TaC_{1-x} \rightleftharpoons \beta\text{-}Ta_2C$
Mo_2C	$1475 \pm 20°$	$\alpha\text{-}Mo_2C + C \rightleftharpoons \beta\text{-}Mo_2C$
W_2C	$2450 \pm 20°$	$\alpha\text{-}W_2C + C \rightleftharpoons \beta\text{-}W_2C$

Figure 14. Differential Cooling Curve of a Tantalum -
33 At% Carbon Alloy

25

evidenced by the recorder trace of a tantalum-carbon alloy with 33 atomic % carbon run under rapid cooling conditions (Figure 14).

D. HIGH TEMPERATURE PHASES IN THE SYSTEMS MOLYBDENUM-CARBON AND TUNGSTEN-CARBON

Apart from the aforementioned phase reaction of the Mo_2C-phase at 1475°C, two other congruently melting phases[3] are formed in this system at high temperatures[36-38]. The DTA-Thermogram of an alloy with 44 atomic % c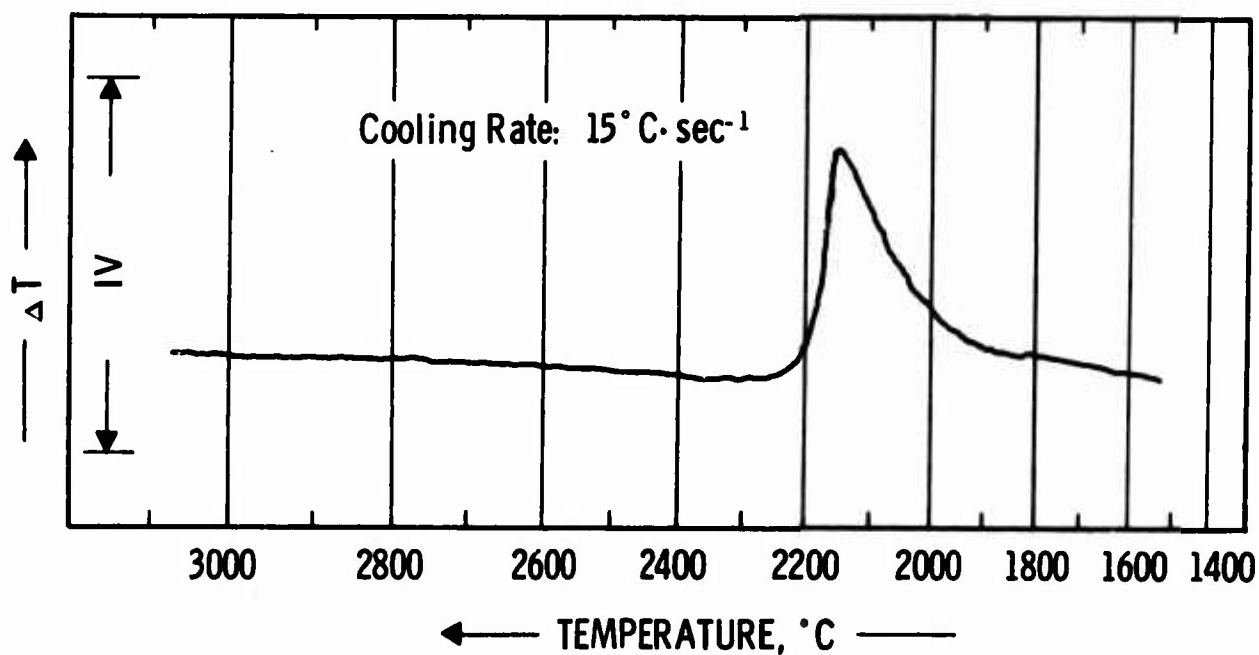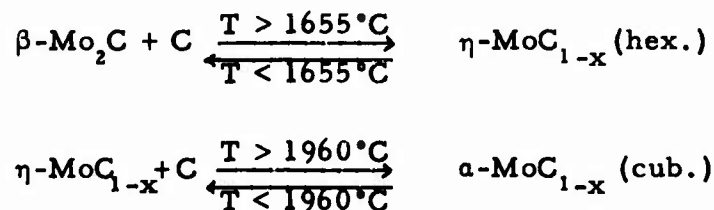arbon (Figure 15) shows the solid state reactions, which are associated with the formation (heating) or decomposition (cooling) of these phases. The overall reactions at the corresponding temperature arrests are:

$$\beta\text{-}Mo_2C + C \xrightarrow[\text{T} < 1655°C]{\text{T} > 1655°C} \eta\text{-}MoC_{1-x}(\text{hex.})$$

$$\eta\text{-}MoC_{1-x} + C \xrightarrow[\text{T} < 1960°C]{\text{T} > 1960°C} \alpha\text{-}MoC_{1-x}(\text{cub.})$$

Melting and solidification of this alloy composition is indicated by the thermal arrests at 2580°C, shown on the heating as well as the cooling cycle. The temperature gap existing between the observed reaction onset for the η-phase on the heating and cooling cycle is due to kinetic effects and the width of this temperature gap approaches zero as the heating or cooling rates are lowered. Very high cooling rates (> 40°C) result in quenching of the η-phase, i.e. no corresponding temperature arrest is observed on the cooling cycle. This effect is not observed with $\alpha\text{-}MoC_{1-x}$, indicating that the decomposition of the cubic high temperature phase proceeds much faster

26
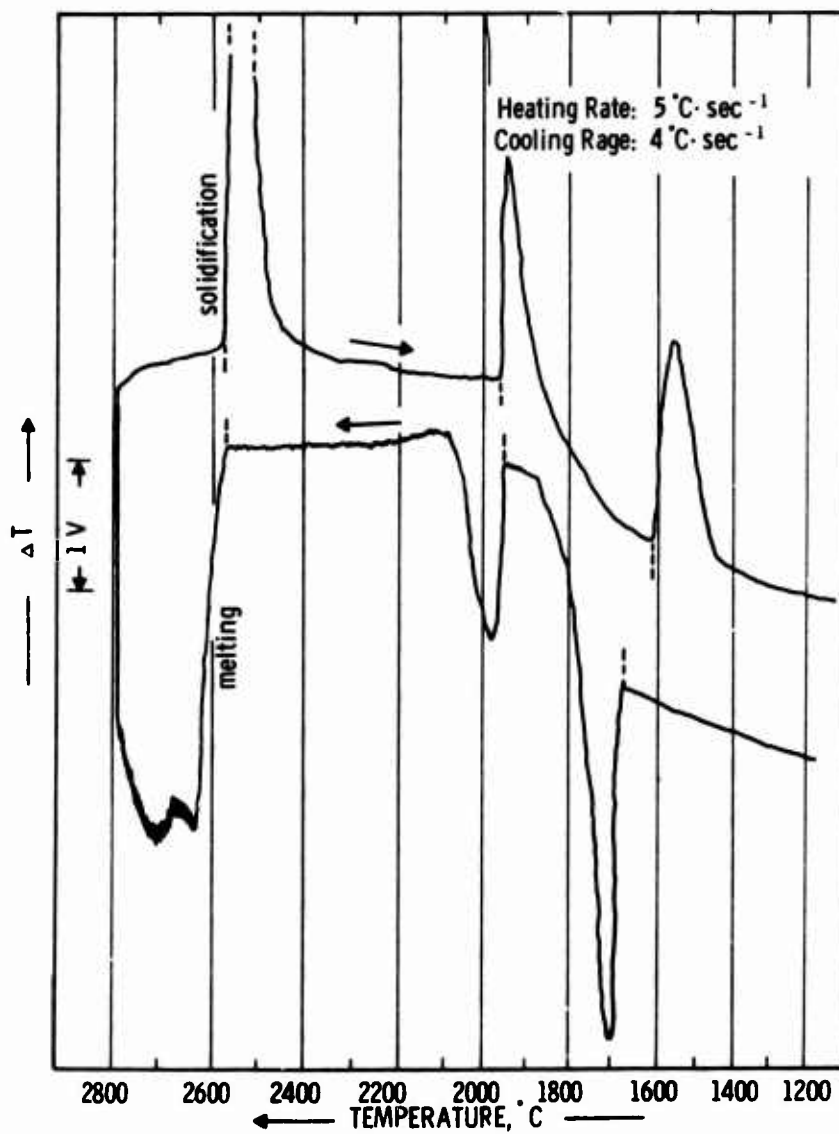
Figure 15.   DTA-Thermogram of a Molybdenum-Carbon
Alloy with 44 Atomic % Carbon

than that of the η-phase. This finding is in accordance with earlier observations[37]. A more detailed study of the decomposition reaction of the $a\text{-MoC}_{1-x}$-phase[3] revealed, that the first reaction product is Mo_2C and graphite, while the equilibrium mixture ($\eta\text{-MoC}_{1-x} \eta$ C) is formed in a consecutive reaction step.
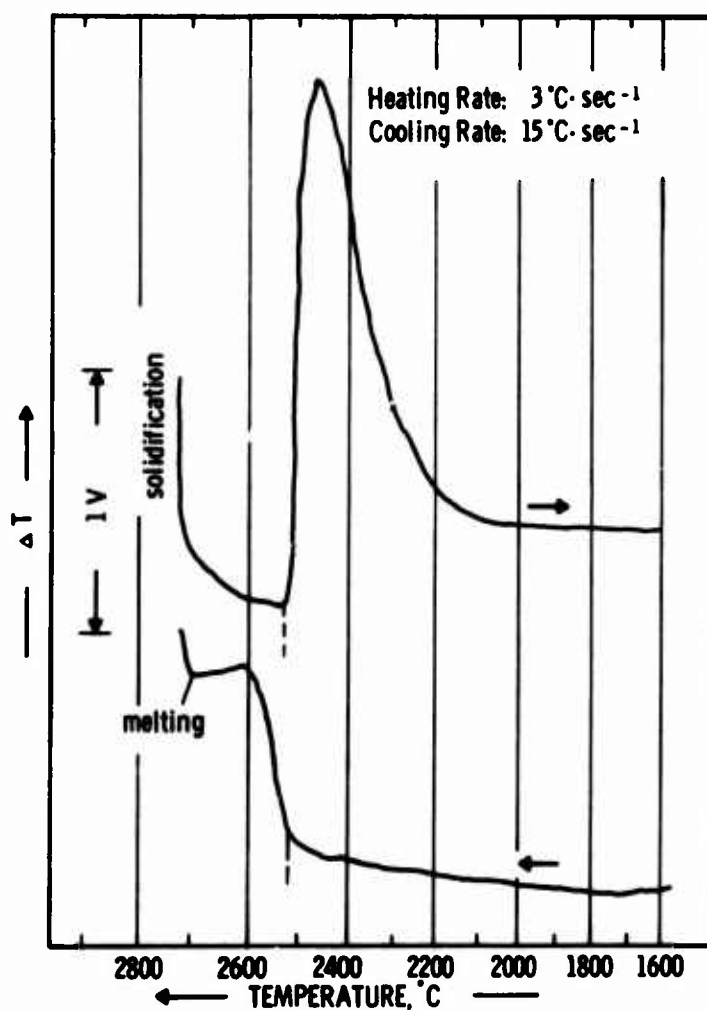
Figure 16. DTA-Thermogram of a Tungsten-Carbon Alloy
(38 At% C), Showing the Formation (Heating) and
Decomposition (Cooling) of the Cubic High
Temperature Phase at 2530°C

28

A phase analogous to the cubic molybdenum carbide is formed in the system tungsten - carbon at high temperatures[39, 40]. The formation (heating) and decomposition (cooling) of this phase at ~2530°C is shown in the DTA-thermogram in Figure 16. Decomposition of the high temperature phase is extremely fast and rapid quenching techniques are necessary to retain it to room temperature[40].
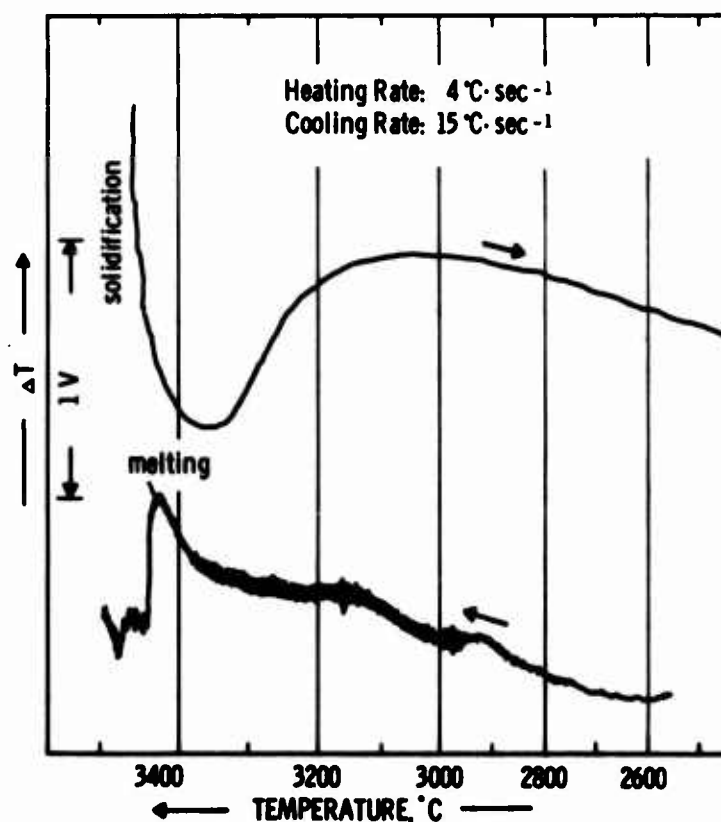
Figure 17. DTA-Thermogram of a Tantalum - 70 At% Carbon Alloy

29

E. PHASE REACTIONS IN BINARY AND TERNARY CARBIDE SYSTEMS

DTA-techniques were also used for the detection and study of rapid precipitation phenomena in substoichiometric tantalum carbide and for the location of eutectic temperatures in refractory carbide systems[33]. An example of the later reaction type is presented in Figure 17, which shows eutectic melting and solidification in a tantalum - 70 At% carbon alloy at 3440°C.

Isothermal reactions in ternary alloys often proceed much more sluggishly than those in unary or binary systems, and also non-equilibrium reactions are more frequently encountered. A close temperature-time control is therefore a necessity for a conclusive interpretation of the results.

The effect of the cooling conditions on the reaction behavior is shown in the DTA-thermograms of a molybdenum-chromium-carbon alloy (Figure 18).

The first thermal arrest, which occurs slightly above 1600°C on the heating cycle is due to the formation of the η-phase, whereas the slight discontinuity observed at 1900°C results from the formation of small amounts of the cubic α-$(Mo,Cr)C_{1-x}$ high temperature phase. Cooling at a rate of 1°C per second shows only a very weak arrest due to the decomposition of the η-phase (shifted to lower temperatures), whereas no apparent delay is encountered in the decomposition of the cubic phase. The X-ray and chemical analysis of the alloy only revealed the presence of the

$(Mo, Cr)_2C$-solid solution and graphite, with only traces of η-phase present.
Both reactions are being quenched at cooling rates in excess of 14°C per
second (lower curve in Figure 18).
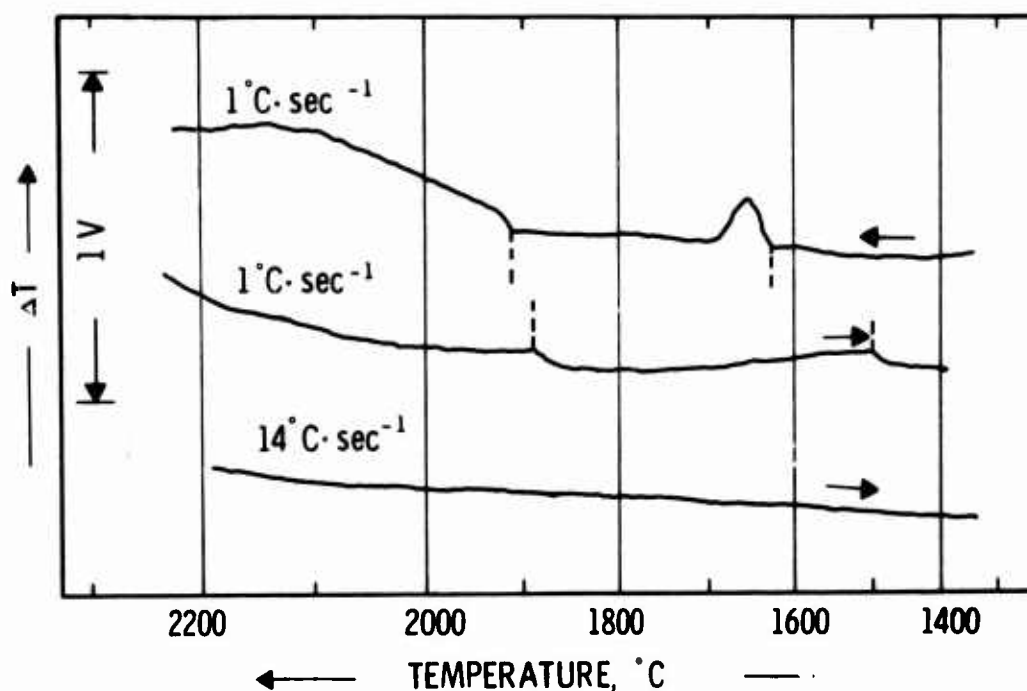
Figure 18. Differential Heating and Cooling Curves of a
Molybdenum-Chromium-Carbon Alloy
(60/5/35 At%) at Different Cooling Rates

Similar conditions are found for dissolution reactions,
for which two examples, showing the disproportionation of cubic mono-
carbide solutions at high temperatures are presented in Figures 19 and 20.

Homogeneous ordering processes are interesting since these reactions do not proceed isothermally, but rather show a gradual change with temperature. However, for the investigation of the thermal effects by DTA-techniques, often use can be made of the fact that a large percentage of the total enthalpy associated with the ordering reaction is delivered within a limited temperature interval.
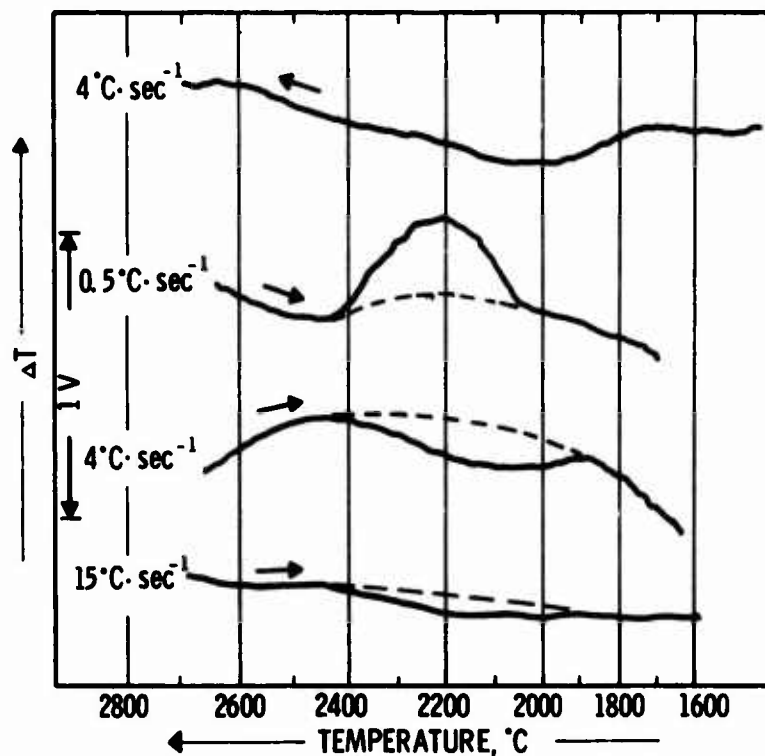
Figure 19. Disproportionation of the Cubic Solid Solution in the System Hf-W-C under Varying Cooling Conditions

Alloy: Hf (40)-W(18)-C(42) At%

A reaction of this type is shown in Figure 21, where in the DTA-thermograms the initiation of a sluggishly proceeding reaction in a $(W, Cr)_{23}C_6$ alloy below 1450°C is indicated. At room temperature,
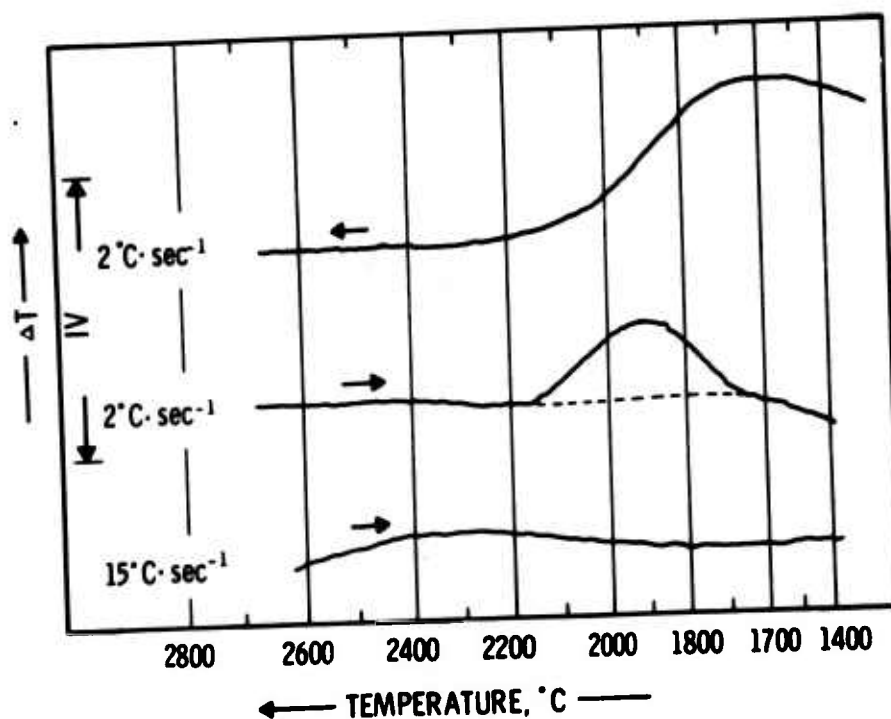
Figure 20.   Disproportionation of the Cubic Carbide Solid
Solution in the System Zr-W-C.
Alloy: Zr(40-W(18)-C(42) At%

substitution of tungsten for chromium in $Cr_{23}C_6$ occurs preferentially at specific point positions[34], but equidistribution over all point positions may be approached at temperatures close to melting.

33

VI.   CONCLUDING REMARKS

The preceding examples show but a few of the possibilities, DTA-techniques can be used for the establishment and elucidation of phase-reactions under temperature conditions, which may not be easily accessible
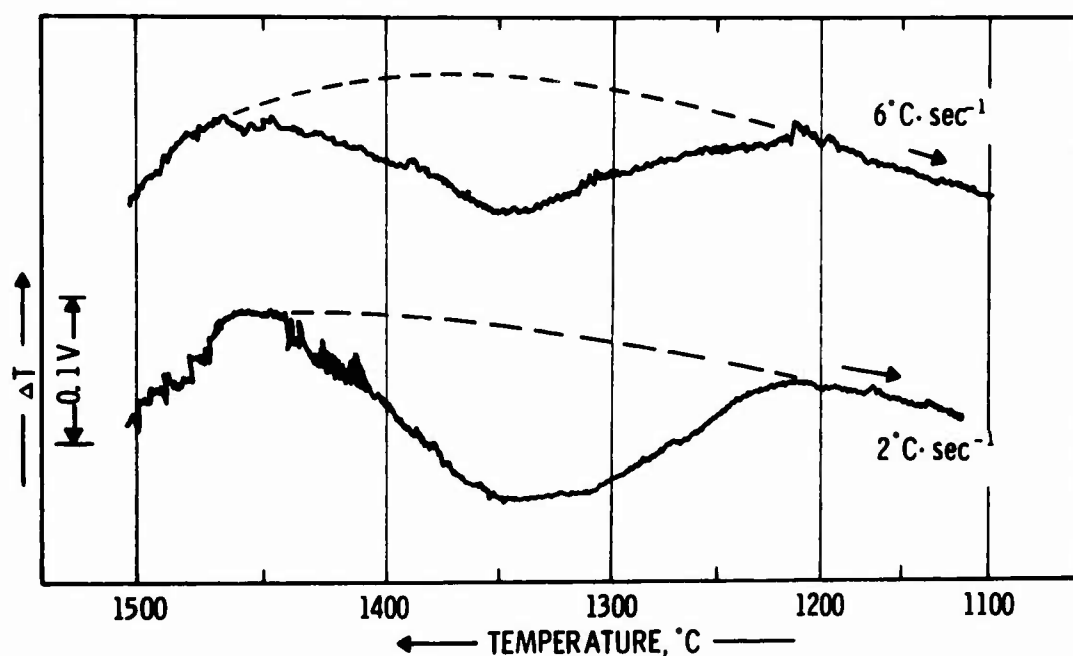
Figure 21.   Differential Cooling Curves of a Tungsten-
Chromium-Carbon (10/70/20 At%) Alloy

by other experimental means.   Although care has to be exercised in the interpretation of the results and the technique does not provide a self-sufficient method, it is a very valuable aid for the accurate establishment of the pure equilibria in complex systems.

REFERENCES

1. E. Rudy and G. Progulski: Planseeber, f. Pulvermetallurgie (in preparation)

2. E. Rudy: Second Progress Report, AF 33(615)-1249 (Oct 1964)

3. E. Rudy, St. Windisch, and Y. A. Chang: AFML-TR-65-2, Part I, Volume I (Jan 1965)

4. H. Le-Chatelier: Compt. Rend. 104 (1887), 1443; Bull.Soc.Franc. Miner 10 (1887), 204

5. W. C. Roberts-Austen: Proc. Inst.Mech.Engrs. (1899). 55

6. E. Saladin: Iron and Steel Metallurgy and Metallography 7 (1904) 237

7. H. Le-Chatelier: Rev. Metall. 1 (1904), 134

8. N.S. Kurnakov: Zhur.Russ. Fiz. Khim.Obshch. 36 (1904), 841
   Z.anorg.Chem. 42 (1904), 184

9. For an exhaustive compilation of earlier work, the following references may be consulted:

   a. L.G. Berg, A.V. Nikolaev, and E. Ya.Rode: "Thermografija", Izv.Akad.Nauk.SSSR, Moscow, 1944

   b. H. Lehmann, S.S. Das, and H.H. Pätsch: "Die Differential-thermoanalyse", Tonind.-Ztg.und Keram. Rundschan, Beiheft 1 (1954)

   c. L.G. Berg: "Trudij Pervogo Soveshchanija po Thermo-grafii (Kazan, 1953)", Izd.Akad.Nauk.SSSR(Moscow and Leningrad, 1955)

   d. M. Elias , M. Stovick, and L. Zahradnik: "Differenči thermickà analysa" (Nakladatelstvi Ceskoslovenske Akad. Věd, Prague, 1957)

   e. R. C. Mackenzie and B. D. Mitchell: Analyst 87 (1962), 420

   f. L. G. Berg: "Introduction to Thermography" (Izd.Akad. Nauk SSSR Moscow 1961).

References (cont'd)

g. J. W. Smothers and Y. Chiang: "Differential Thermal Analysis" (Chemical Publishing Company, New York, 1958).

h. C. B. Murphy: Anal. Chem. $\underline{32}$ (1960), 168

10. C. Sykes: Proc. Roy. Soc. $\underline{148}$ (1935), 422

11. K. G. Kumanin: Zh. Prikl. Khim. $\underline{20}$ (1947), 1242

12. C. Eyraud: Compt. Rend. $\underline{240}$ (1955), 862

13. E.S. Watson, M. J. O'Neill, J. Justin and N. Brenner: Analyt. Chem. $\underline{36}$ (1964), 1233

14. T. F. Newkirk: J. Am. Ceram. Soc. $\underline{41}$ (409) 1958

15. H. J. Borchardt: Private communication, quoted by C.B. Murphy (ref. 9h)

16. M. M. Hopkins: Rev. Sci. Instr. $\underline{35}$ (1964), 1658

17. J. M. Pakulak and G.W. Leonard: Anal.Chem. $\underline{31}$ (1959), 1037

18. R.V. Sara and R.T. Dolloff: WADD Tr 60-143, Part III (1962)

19. S. Langer, General Atomic, San Diego: Private Communication 1961 and 1963

20. G. N. Rupert: Rev. Sci. Instr. $\underline{34}$ (1963), 1183

21. D. K. Deardorff and H. Kato: Trans AIME $\underline{215}$ (1959), 876

22. N. J. Grant and B.C. Giessen: WADD 60-132 (1960)

23. J. D. Fast: J. Appl. Phys. $\underline{23}$ (1952), 350

24. A. Taylor and N.J. Doyle: J. Less Common Metals, $\underline{7}$ (1964), 37

25. R.G. Ross and W. Hume-Rothery: J. Less-Common Metals, $\underline{5}$ (1963), 258

26. C. Zwikker: Physica $\underline{6}$ (1926), 361

References (cont'd)

27.   P. Duwez: J. Appl. Phys. $\underline{22}$ (1951), 1174

28.   E. Rudy and P. Stecher: J. Less-Common Metals, $\underline{5}$ (1963), 78

29.   E. Rudy and P. Stecher: Unpublished work 1962

30.   M. I. Copeland in : USB-U-952 (U.S. Bureau of Mines, 1962)

31.   R.V. Sara and G. E. Lowell: WADD-TDR-60-143, Part V, (1964)

32.   R. G. Avarbe, A.I. Augustinnik, Yu. N. Vilk, Ya.D. Konraskov,
       S.S. Nikolskii, Ya. A. Oneichenko, and S.S. Ordanjan: J. Appl.
       Chem. USSR, $\underline{35}$ (1962), 1899-1902

33.   E. Rudy, C. E. Brukl and D. Harmon: Work under AF 33{614)-1249
       1964 (to be published)

34.   A. Westgren A: Nature, $\underline{132}$ (1933), 480

35.   E. Rudy and Y.A. Chang: Paper presented at the V. Plansee
       Seminar, Reutte, Tirol, 1964 (Plansee Proc. 1965, in print).

36.   H. Nowotny, E. Parthe, R. Kieffer and F. Benesovsky: Mh. Chem
       $\underline{85}$ (1954), 255

37.   E. Rudy, El. Rudy, and F. Benesovsky: Planseeber, Pulvermet.
       $\underline{10}$ (1962), 42

38.   E. V. Clougherty, K. H. Lothrop, and J.A. Kafalas: Nature, $\underline{191}$
       (1961), 1194

39.   K. Kirner: Private communication 1957, quoted by R. Kieffer and
       F. Benesovsky, Hartstoffe (1963)

40.   R.T. Dolloff and R.V. Sara: WADD TR-60-143 (1961), Part II

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*	2a. REPORT SECURITY CLASSIFICATION
Aerojet-General Corporation Materials Research Laboratory Sacramento, California	Unclassified
	2b. GROUP N.A.

3. REPORT TITLE

Ternary Phase Equilibria in Transition Metal-Boron-Carbon-Silicon Systems
Part III. Special Experimental Techniques. Volume I: High Temperature Differential Thermal Analysis

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5. AUTHOR(S) *(Last name, first name, initial)*

H.D. Heetderks
E. Rudy
T. Eckert

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
August 1965	37	40

8a. CONTRACT OR GRANT NO. AF 33(615)-1249	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. 7350	AFML-TR-65-2 Part III, Vol. I
c. Task No. 735001	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	N.A.

10. AVAILABILITY/LIMITATION NOTICES

Qualified requesters may obtain copies of this report from DDC

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	AFML (MAMC) Wright-Patterson AFB, Ohio 45433

13. ABSTRACT

A high sensitivity differential thermal analysis apparatus, capable of operating to temperatures of 3600°C under controlled time-temperature conditions, is described.

Measurements on binary and ternary carbide systems revealed a number of previously undetected phase reactions. With the exception of V_2C, all subcarbides of the refractory transition metals undergo isothermal phase changes at high temperatures. The lower temperature stability limits of the high temperature phases in the systems Mo-C and W-C were determined. Similar to the corresponding system with oxygen, the α-modification of hafnium is stabilized to higher temperatures by carbon additions, while the α-β-transformation in titanium and zirconium is affected to a moderate extent only.

The application of DTA-techniques to the investigation of non-variant equilibria involving a liquid phase and to the study of reaction kinetics (disproportionation of solid solutions, reactions along non-equilibrium paths, reactions involving order-disorder phenomena) is discussed and examples are given.

DD ,FORM 1473
1 JAN 64

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Phase Equilibria Experimental Techniques High Temperature Differential Thermal Analysis						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through

_____ ."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through

_____ ."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through

_____ ."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.